The Microscope as an Aid to Organic Chemistry

ORGANIC chemistry and chemical microscopy may be termed "the twin sciences." They were introduced to the world together by Raspail just a century ago in his book, *Organic Chemistry by a New Method of Observation*. But, as is often the case with brothers, these two have pursued different courses. Organic chemistry, under the tutelage of its godfather, Berzelius, began the slow, steady development that has finally placed it among the leaders in the scientific list, while on the other hand, microscopy became lost for the most part with only now and then a word of its doings from foreign fields.

In the 1860's, however, microscopy flashed into momentary prominence in the work of the toxicologist, Wormley, as a method for identifying poisons. Shortly thereafter it was adopted by the petrographers, and its optical properties were extended. Then it became entrenched in the front line of Pasteur's war on disease, and ever since has been regarded as the symbol of the biological sciences. More recently it has proved of great value to the metallographic arts, and its varied career now is being expanded through use by the legal profession in its war on crime, in the guise of forensic ballistics.

Organic chemists also are finding that the microscope in its present advanced state of development can be made one of the most useful and versatile tools in their laboratory. So, after a separation of a century, the brothers are again becoming united, to their mutual advantage.

Economy of Time and Materials

The value of the microscope to the chemist is not primarily based on its economies of materials and reagents, but on its ability to conserve time. Through its use the worker can save hours of analytical effort by a few simple and well-directed observations during the course of his experiments.

From the first contact with a crude material to the final examination of the finished product, the microscope is a versatile assistant to the chemist. Its principal uses may be divided into three general classes: (*1*) preliminary examinations, (*2*) qualitative tests for the presence of acid and basic radicals, and (*3*) determination of the optical constants of organic materials.

The preliminary examination can give immediate and essential information concerning the number and nature of components in a mechanical mixture. In the case of raw natural products, the

various units may have such a characteristic appearance that they can be recognized by simple observation of the material spread out on a slide. In such a situation the percentage composition often may be estimated with a high degree of accuracy without resorting to more elaborate analyses.

Analysis of Mixtures

If, instead of components easily recognized, the material consists of a mixture of powdered crystalline materials, ground so as to destroy any characteristic form, the microscope becomes still more important. A melting point by the usual methods would be of no value, yet in a micro-apparatus the melting points of one or a dozen particles, made simultaneously, may give definite information concerning the material. The difference in optical character of the fragments in the mixture under polarized light, a difference in their principal refractive indices, or a combination of these, may provide simple, rapid, and positive grounds for distinguishing the number and type of the components. Each component may then be separated, a few crystals being sufficient, and their solubilities in a number of solvents determined as a preliminary to the usual methods. Such information, while not conclusive in itself, many times provides an invaluable basis from which to continue the investigation.

Precipitation Reactions

The qualitative phase of chemical microscopy is based primarily upon characteristic precipitation reactions. This was the basis of Wormley's work on the microchemistry of poisons. He found that the precipitated salts of the alkaloids had distinctive microscopic appearances which could be used to establish their identity. Cole [PHIL. J. OF SCI. *22*, p. 631 (1923)] describes the results of a large number of experiments with hexamethylenetetramine as a re-

agent for metallic salts of which about ten were sufficiently characteristic to identify the metal. Conversely, this method is equally efficient as a test for hexamethylenetetramine. The literature on this type of procedure is practically complete for inorganic materials and is comprehensive for certain classes of materials, such as the alkaloids, in the field of organic chemistry.

Optical Constants of Crystals

Useful and labor-saving as the foregoing applications may be, the unique contribution of microscopy to organic chemistry lies in the determination of the optical constants of a crystal. When viewed between the crossed nicols of a petrographic microscope, a crystal will be either colorless in any position—isotropic—or it will exhibit more or less brilliant polarization colors—anisotropic. An isotropic crystal has the same refractive index in any direction that light passes through it. This may be determined very simply by immersion methods. If anisotropic, and the stage is rotated, the color will disappear—extinguish—at positions 90° apart. If this position is parallel to the plane of vibration of the nicols, as indicated by the cross hairs and the long axis or side of the crystal, this fact is noted; if it is in some other position, the angle formed by the edge of the crystal and the nearest cross hair is measured. This is the extinction angle.

With a modern petrographic microscope, determination of other properties such as whether the crystal is uniaxial or biaxial, measurement of the optic axial angle, and establishment of the refractive index exhibited along each optic axis, may be accomplished. These recorded numerical constants form the Bertillon system of the world of organic crystalline materials. When these values are known for any compound, it can be identified wherever encountered.

An Anti-Creep Distillation Flask

CERTAIN organic compounds, especially those that boil at high temperatures, such as benzidine, alpha-naphthylamine, acetyl alpha-naphthylamine, and benzenesulfonyl chloride, exhibit a marked tendency to "creep" when distilled under reduced pressure.

This creeping is due in part to the pushing action of the vapor stream on the liquid which condenses on the walls parallel to the direction of flow. Modifying the neck of the distillation flask in such a manner as to break the continuity of the walls, or to change the parallel relationship between the vapor stream and the liquid, materially retards this tendency.

In our laboratory this creeping has been overcome satisfactorily by inserting a comparatively large bulb in the side neck of a modified Claisen flask so that the vapor escapes at right angles to the entrance. The intervening concave surface of the bulb constitutes the necessary break in the parallel relationship between the glass walls and the course of the vapor stream. Also, the eddy currents caused by the vapor striking the wall opposite tend to sweep the condensate on the surface of the bulb back toward the distillation flask.

When distilling compounds that have high melting points, it is necessary sometimes to warm the secondary flask with a small flame until the distillation gets under way.

The set-up in the accompanying illustration shows a 3-liter distillation flask with a 1-liter bulb. On the basis of actual performance the approximate ratio of 3 to 1 has been found to be most satisfactory.
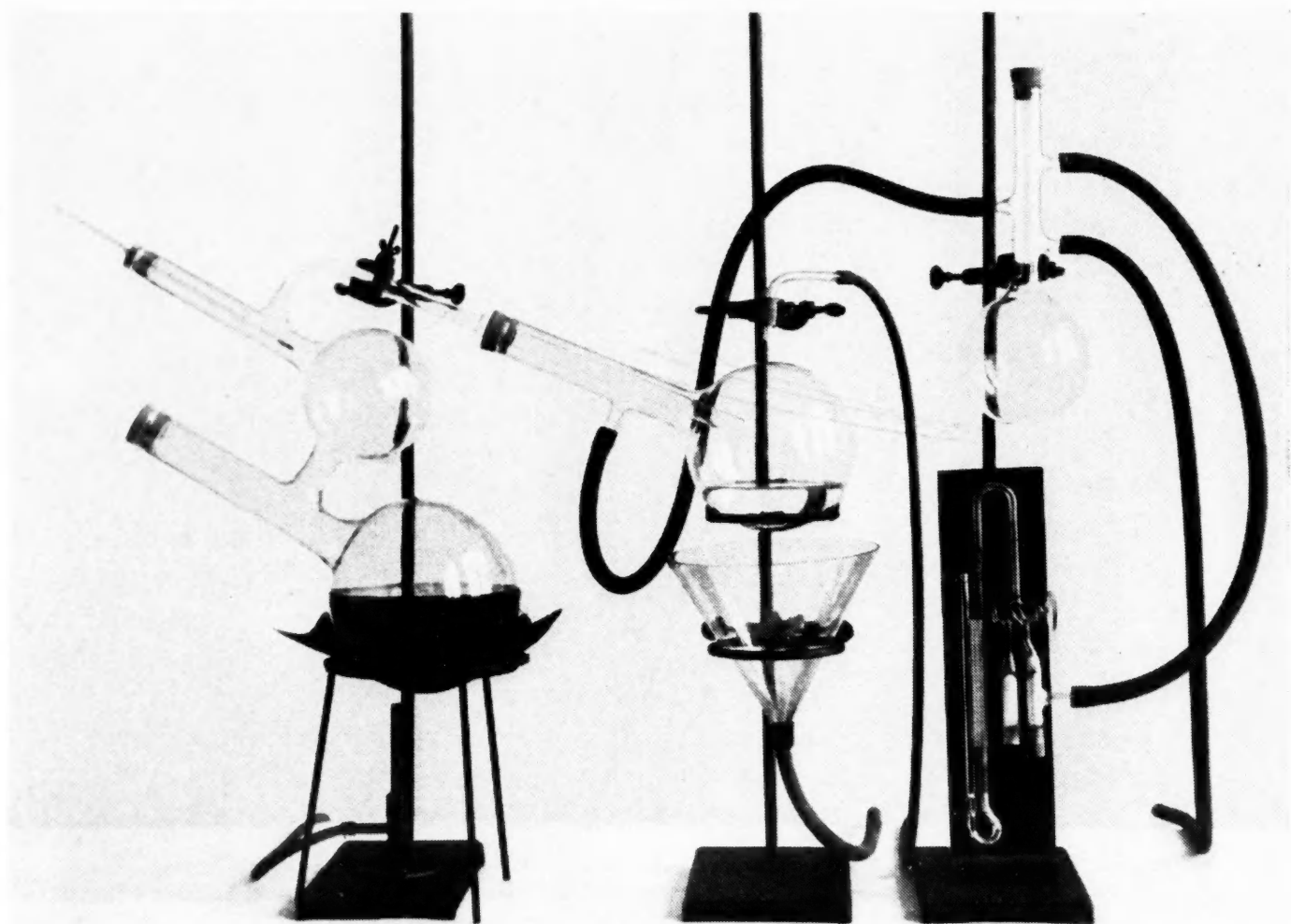
Anti-creep distillation flask as used in the final purification of benzenesulfonyl chloride.

Eastman Organic Chemicals as Analytical Reagents

XXIX Reagents for Platinum and Palladium

p-DIMETHYLAMINOBENZALRHODANINE

Feigl, Krumholz, and Rajmann, MI-KROCHEMIE *3*, 165 (1931)

Palladous salts give a dark violet precipitate with a solution of dimethylaminobenzalrhodanine. Platinum and iridium yield similar precipitates, but not so readily. Methods also are given for detecting palladium in the presence of gold and silver.

DIMETHYLGLYOXIME

Graulich, CHEM. ABSTRACTS, *24*, 1599 (1930)

Palladium is determined in precious metal alloys by dissolving the metal in aqua regia, diluting with water, and then adding dimethylglyoxime solution. The precipitate is washed, dried at 120° C., and weighed. For platinum, the aqua regia solution is diluted with one and one-half parts of water and heated for an hour with ammonium chloride and dimethylglyoxime. The precipitate is filtered, washed with ammonium chloride solution, ignited, and weighed.

FORMIC ACID

Treadwell-Hall, ANAL. CHEM., Vol. II, p. 249 (1928)

The platinum solution is neutralized with ammonia, treated with formic acid and ammonium acetate, and finally refluxed for twenty-four hours. The reduced metal is then filtered, washed, dried, ignited, and weighed.

6-NITROQUINOLINE

Ogburn and Riesmeyer, J. A. C. S. *50*, 3018 (1928)

A hot aqueous solution of 6-nitroquinoline precipitates palladium in the form of a thick, flocculent yellow compound. This is washed, dried, and finally converted to metallic palladium. Platinum and other metals of the platinum group are not precipitated by the reagent.

Thirty-five New Eastman Organic Chemicals

The following chemicals recently have been added to our stock. Prices and purity specifications of these compounds will be found in the new List No. 24 of Eastman Organic Chemicals, which has just been issued.

Acetonylacetone
Acetylbenzoyl
Acetylcaproyl
Allyl n-Caproate
2-Aminoresorcinol Hydrochloride
Arachidic Acid
Azelaic Acid
p-Chloroanisole
1.3-Diaminopropanol
1-Diethylamino-2.3-propandiol
2.5-Dimethylfuran
2.5-Dimethylpyrrole
2.5-Dimethylthiophene
2.4-Dinitrodiphenylamine
Epibromohydrin
Epichlorohydrin
2-Furoic Anhydride
Gluconic Acid
Glycerol $\alpha.\gamma$-Dibromohydrin
Hexabromoethane
m-Hydroxybenzaldehyde
Methyl p-Aminobenzoate
m-Nitrobenzyl Alcohol
o-Nitro-p-chlorophenol Sodium Salt
iso-Nitrosomethyl-n-hexyl Ketone
iso-Nitrosomethyl-n-propyl Ketone
Pentachlorophenol
iso-Quinoline
Suberic Acid
1.3.5-Triaminobenzene Trihydrochloride
2.4.6-Triaminobenzoic Acid
2.4.6-Triaminochlorobenzene Trihydrochloride
2.4.6-Triaminotoluene Trihydrochloride
Triphenylacetic Acid
Triphenyltin Chloride